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Компьютерное квантово-химическое моделирование взаимодействия фосфата магния с незаменимыми аминокислотами

Computer quantum chemical simulation of the interaction of magnesium phosphate with essential amino acids

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Аннотация. *В рамках данной работы было проведено компьютерное квантово-химическое моделирование взаимодействия фосфата магния с незаменимыми аминокислотами с целью определения оптимального стабилизатора для наночастиц $Mg_3(PO_4)_2$. Квантово-химическое моделирование проводилось с использованием программного обеспечения QChem и молекулярного редактора IQmol. На первом этапе проводилось моделирование молекулы фосфата магния и молекул незаменимых аминокислот, далее рассматривалось моделирование молекулярного комплекса «аминокислота-$Mg_3(PO_4)_2$», в котором взаимодействие фосфата магния с аминокислотой проходило через ионизированную аминогруппу. В результате получены модели молекулярных комплексов, а также рассчитаны значения полной энергии молекулярного комплекса, энергии высшей заселённой и низшей свободной молекулярных орбиталей, химической жёсткости и разницы полной энергии аминокислоты и молекулярного комплекса «аминокислота-$Mg_3(PO_4)_2$». В результате установлено, что незаменимые аминокислоты могут быть эффективными стабилизаторами для наночастиц фосфата магния, что подтверждается значениями разницы полной энергии и химической жёсткости молекулярных комплексов. В связи с тем, что молекулярный комплекс триптофана и фосфата магния, в котором взаимодействие молекул происходит через аминогруппу в индольном кольце триптофана, обладает наибольшими значениями разницы полной энергии (ΔE = 1946,223 ккал/моль) и химической жёсткости (η = 0,121 эВ), можно сделать вывод, что триптофан является оптимальным стабилизатором для наночастиц фосфата магния.*

Ключевые слова: компьютерное квантово-химическое моделирование, незаменимые аминокислоты, наночастицы фосфата магния, триптофан, химическая жёсткость

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Abstract. *As part of this work, a computer quantum chemical simulation of the interaction of magnesium phosphate with essential amino acids was carried out in order to determine the optimal stabilizer for $Mg_3(PO_4)_2$ nanoparticles. Quantum chemical modeling was carried out using the QChem software and the IQmol molecular editor. At the first stage, the modeling of the magnesium phosphate molecule and the molecules of essential amino acids was carried out, then the modeling of the molecular complex "amino acid- $Mg_3(PO_4)_2$" was considered, in which the interaction of magnesium phosphate with an amino acid passed through an amino group. As a result, models of molecular complexes were obtained, and the values of the total energy of the molecular complex, the energies of the highest populated and lowest free molecular orbitals, chemical rigidity and the difference in the total energy of the amino acid and the molecular complex "amino acid- $Mg_3(PO_4)_2$" were calculated. As a result, it was found that essential amino acids can be effective stabilizers of magnesium phosphate nanoparticles, which is confirmed by the values of the difference in total energy and chemical rigidity of molecular complexes. Due to the fact that the molecular complex of tryptophan and magnesium phosphate, in which the interaction of molecules occurs through the amino group in the in the indole ring of tryptophan, has the highest values of the difference in the total energy (ΔE = 1946,223 kcal/mol) and chemical hardness (η = 0.121 eV), it can be concluded that tryptophan is the optimal stabilizer for nanoparticles magnesium phosphate.*

Keywords: computer quantum chemical modeling, essential amino acids, magnesium phosphate nanoparticles, tryptophan, chemical hardness

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Introduction. Magnesium is one of the essential macroelements - substances necessary for humans and not synthesized by the body. This metal is an important component of the functioning of the nervous system, is involved in protein synthesis, and also supports the functioning of the heart. In the human body, magnesium is mainly found in bones, muscle and other tissues. Thus, the body of an adult weighing 70 kg contains about 24 g of magnesium [1]. Despite the low content in hard tissues (0.44 % wt. in enamel, 1.23 % wt. in dentin, 0.5 – 0.9 % mass in bone), Mg^{2+} plays an important role in their mineralization. Magnesium affects the vascular tone of peripheral and coronary vessels, and is also involved in the activation of enzymes and muscle contractions, transmission of impulses at neuromuscular synapses, platelet aggregation, and metabolic processes in tissues with ischemia [2, 3].

Since magnesium is an essential macronutrient, its concentration in the human body must be maintained by consuming foods and medications containing magnesium. As a result of *Muth's* and *Maathuis's* research it was found that magnesium entering the human body with food is absorbed only by 40 % [4, 5]. Magnesium travels a long way from absorption in the gastrointestinal tract to entering the blood and distribution throughout the body: about 60% accumulates in the bones, about 20 % – in skeletal muscles, 19 % – in other soft tissues, less than 1 % is outside the cells, and only a part of this percentage circulates in the blood. Due to a lack of magnesium in the human body, hypomagnesemia develops, the development of which leads to disruption of the cardiovascular system, muscle cramps, and increased anxiety. [6, 7].

Magnesium deficiency occurs due to malnutrition, diseases of internal organs and disruption of the endocrine system [8].

To increase the proportion of absorbable magnesium in the human body, various preparations containing magnesium compounds, such as magnesium citrate, oxide, malate or glycinate, are used today [9, 10]. The most effective form of magnesium presented today is citrate with a degree of digestibility of 90 % [11, 12]. The use of nanosized forms of magnesium is a promising direction for increasing the digestibility of this macroelement, since they have greater biocompatibility with the human body and do not have a toxic effect on the body [14, 15]. At work *Sengupta J.* The biocompatibility of magnesium nanoparticles and their effect on the human body was considered, as a result of which it was revealed that the degree of digestibility of the nano-sized form of magnesium is at least 90-95 % [15].

Stabilization of nanoparticles is one of the ways to obtain nanomaterials with certain properties and sizes. To stabilize nanoparticles, various methods are used, such as maintaining a certain *pH level* and using various surfactants [16, 17]. One of the promising methods for stabilizing nanoparticles of macro and microelements is the use of amino acids, thanks to which it is possible to obtain substances necessary for the human body, combined in one preparation and with high biological digestibility [18 – 20]. Using modern computer modeling methods, it is possible to obtain theoretical information about the process of stabilization of nanoparticles, on the basis of which a holistic picture of the properties of the compounds under study is formed [21, 22].

Thus, the purpose of this work is to conduct computer quantum chemical modeling of the interaction of magnesium phosphate with essential amino acids to determine the optimal stabilizer for $Mg_3(PO_4)_2$ nanoparticles.

Materials and research methods. *QChem* software using a molecular editor - *IQmol* , using the Hartree Fock (*HF*) method and the *6-31 G basis* .

Computer modeling was carried out in two stages: at the first stage, individual molecules of magnesium phosphate and essential amino acids – *L* -valine (Val*)*, *L* -leucine (*Leu*), *L* -isoleucine (*Ile*), *L* -methionine (*Met*), *L* -threonine (*Tre*), *L* -lysine (*Lys*), *L* -phenylalanine (*Phe*), *L* -tryptophan (*Trp*); Next, modeling of the interaction of magnesium phosphate with amino acids through the amino group was carried out. As a result, molecular models, electron density distribution, highest occupied and lowest unoccupied molecular orbitals were obtained. Also, as calculated simulation results, the values of the total energy of the molecular system (E), the energy of the highest occupied molecular orbital (E_{HOMO}), and the energy of the lowest free molecular orbital (E_{LUMO}) were obtained. Based on the data obtained, the difference in the total energy of the amino acid and the system of interaction of magnesium phosphate with the amino acid (ΔE) and the chemical hardness (η) were calculated, calculated using formulas 1 – 2 [23, 24]:

$$\Delta E = E_0 - E_1, \quad (1)$$

where E_0 is the total energy of the amino acid molecule,

E_1 – total energy of the system of interaction of magnesium phosphate with amino acid.

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2}. \quad (2)$$

Research results and their discussion. As a result of computer modeling of the interaction of magnesium phosphate with essential amino acids, quantum chemical calculations were obtained, presented in Table 1.

Table 1 – Results of computer quantum chemical simulation of the interaction of magnesium phosphate with essential amino acids

Molecular system	Reaction $Mg_3(PO_4)_2$ with amino acid	E, kcal/mol	$EHOMO$, eV	$ELUMO$, eV	η, eV	ΔE, kcal/mol
$Mg_3(PO_4)_2$	–	-1873.591	-0.339	-0.075	0.132	–
Val	–	-402.112	-0.249	0.016	0.133	–
Val - $Mg_3(PO_4)_2$	Via the α-amino group of valine	-234 7,545 _	-0.171 _	- 0.047 _	0.062	1945.433
Leu	–	-441.397	-0.260	0.006	0.133	–
Leu - $Mg_3(PO_4)_2$	Through the α-amino group of leucine	- 238 7,046 _	-0.181 _	- 0.0 05	0.088	1945.649
Ile	–	-441.394	-0.247	0.018	0.133	–
Ile - $Mg_3(PO_4)_2$	Through the α-amino group of isoleucine	-238 6,594 _	-0.137 _	0.0 43	0.090	1945,200
Met	–	-800.251	-0.232	0.006	0.119	–
Met - $Mg_3(PO_4)_2$	Through the α-amino group of methionine	- 2745.140	-0.183 _	0.0 37	0.110	1945,889
Tre	–	-438.015	-0.248	0.006	0.127	–
Tre - $Mg_3(PO_4)_2$	Through the α-amino group of threonine	- 238 3,285 _	-0.225 _	- 0.0 35	0.095	1945.270
Lys	–	-496.481	-0.177	-0.024	0.077	–
Lys - $Mg_3(PO_4)_2$	Through the α-amino group of lysine	- 2442.306	-0.228 _	-0.0 21	0.104	1945.825
	Through the ε-amino group of lysine	- 2441.983	-0.215 _	- 0.0 47	0.084	1945.502
Phe	–	-554.424	-0.240	0.002	0.121	–
Phe - $Mg_3(PO_4)_2$	Through the α-amino group of phenylalanine	- 2500.402	-0.199 _	- 0.0 08	0.096	1945,978
Trp	–	-685.684	-0.195	-0.035	0.080	–
Trp - $Mg_3(PO_4)_2$	Through the α-amino group of tryptophan	- 2630.871	-0.209 _	- 0.0 24	0.093	1945.187
	Through the amino group in the indole ring of tryptophan	- 263 1,907 _	-0.243 _	- 0.0 01	0.121	1946.223

As a result of the analysis of the data obtained, it was established that the interaction of magnesium phosphate with amino acids is energetically favorable, which is confirmed by the values of the difference in total energy ($\Delta E > 1945$ kcal/mol), which is also greater than the total energy of a magnesium phosphate molecule. Also, molecular complexes "amino acid- $Mg_3(PO_4)_2$" are chemically stable ($\eta \geq 0.062$ eV). Based on this, we can conclude that amino acids can be effective stabilizers for magnesium phosphate nanoparticles.

Also, based on the results obtained, the optimal stabilizer for magnesium phosphate – tryptophan – was determined. The model of the molecular complex " *Trp* - $Mg_3(PO_4)_2$ ", the electron density distribution, as well as the highest occupied and lowest unoccupied molecular orbitals are presented in Figure 1.

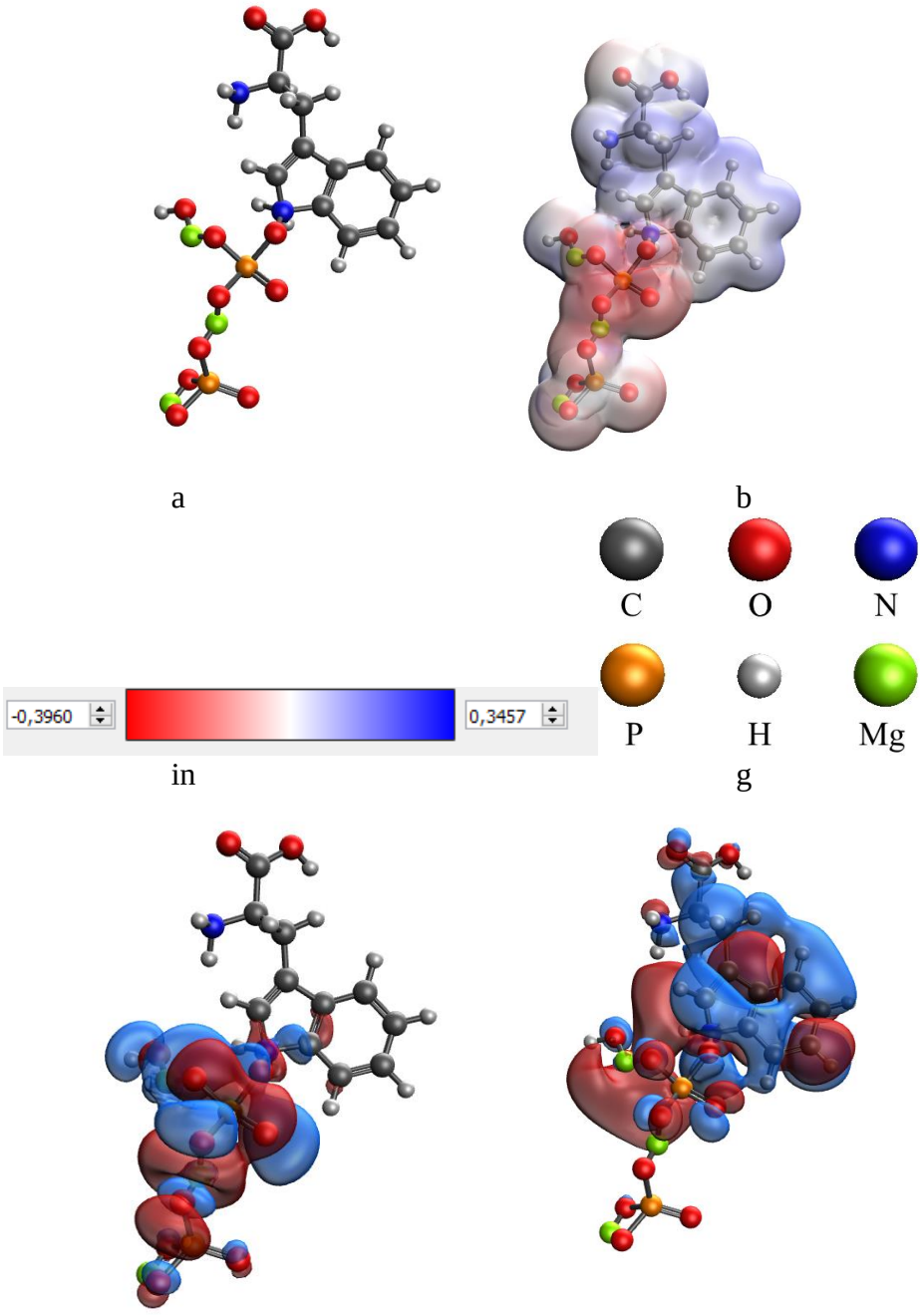

Figure 1 –Results of modeling the molecular complex " Trp - $Mg_3(PO_4)_2$ ", in which the interaction of tryptophan and magnesium phosphate occurs through the amino group in the indole ring of tryptophan a – model of a molecular complex; b – electron density distribution; c – gradient of electron density distribution; d – decoding of atoms; e – highest occupied molecular orbital; e – lowest free molecular orbital

The resulting molecular complex has the largest energy difference (ΔE = 1946.223 kcal/mol) and chemical hardness (η = 0.121 eV), which indicates the energetic benefit of the interaction of tryptophan with magnesium phosphate through the amino group in the indole ring of tryptophan, as well as the high chemical stability of this molecular complex.

Conclusion. As a result of computer quantum chemical modeling of the interaction of magnesium phosphate with essential amino acids, models of molecular complexes "amino acid-$Mg_3(PO_4)_2$" were obtained, the values of the total energy of the molecular complex, the energy of the highest occupied and lowest free molecular orbitals were obtained, and the values were calculated chemical rigidity of the system and the difference in the total energy of the amino acid and the molecular complex. Based on the data obtained, it was established that

essential amino acids can be effective stabilizers for magnesium phosphate nanoparticles. It has also been established that the molecular complex " *Trp - $Mg_3(PO_4)_2$* ", in which the interaction of tryptophan with magnesium phosphate occurs through the amino group in the indole ring of tryptophan, is the most energetically favorable and chemically stable.

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